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Rheological and mechanical properties of filled with calcite concentrate polypropylene blends

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Abstract. It has been found that the addition of calcite concentrate 5-50% w/w allows regulation the rheological properties of polypropylene-based composition melts. It was established that the increasing of the amount of the filler up to 50% w/w in the PP based composition led to decrease of its melt viscosity by 40% comparing with initial polymer melt. This may be explained by the plasticization effect of stearic acid, which is commonly used to treat the surface of calcite concentrate. The addition of a propylene-octene block copolymer as a modifying additive makes it possible to produce high-filled materials that are more resistant to impact loading. The increasing the calcite concentrate content up to 10% w/w increases the impact strength by 10% compared with the initial polypropylene. Further increasing of calcite concentrate content up to 20 % led to decrease impact strength almost to the value for the initial polypropylene, at not critical decrease in tensile strength. Elongation of compositions is higher with the presence of block copolymer. The developed compositions with propylene-octene block copolymer as a modifying additive can be used for production of automotive details.

Introduction

Modern polymer composite materials are multicomponent systems. The addition of mineral fillers in polymers makes it possible to develop materials with required performance properties and contributes to cost reduction [1]. Products, which made from mineral-filled plastics, are widely used in the automotive industry [2], in the construction industry [3], for anticorrosive coatings of pipelines [4], in the production of medical supplies [5], sports coverings [6] and consumer goods [7]. The main problem, as a rule, is the reduction of strength and technical characteristics when the amount of filler in the compositions is increased. Srivabut et al. [8] studied the effect of filling with nano-clay, talc and calcium carbonate on polypropylene (PP) already filled with wood flour. It was reported that samples containing 7% w/w of calcium carbonate were characterized by optimal physical and mechanical properties. One of the directions of development of the materials with increased impact resistance is a modification of the filled polymers adding elastomers [9]. Nguen et al. [10] have shown that the modification of PP by a metallocene ethylene-propylene elastomer leads to a significant increase of the impact strength and elongation at break, however, the modulus of elasticity and the yield stress decrease.

The addition of fillers and elastomers not only affects the performance properties of polymer material, but also its processing ability. The main technological factor determining the way of processing is the fluidity of the composition [11]. The filling always leads to products' molding difficulties due to the increase of the viscosity of the melt [12]. Compositions [13] based on PP and ethylene-propylene rubber, which meet the technical characteristics of the bumpers and other parts of cars, characterized by high impact strength have been developed; however, the melt flow rate of such mixtures reaches only 3-6 g/10 min.



A knowing of rheological properties allows an estimation of the effect of composition components on the properties of the composition melt [14]. The melts of the filled polymers can be considered as concentrated suspensions. For such systems, it is reasonable to take into account the possibility of interaction between the particles, which affects the nature of the flow. It is known that the properties of such polymer compositions are determined by the content of the filler, the size and degree of aggregation of the particles, as well as the surface characteristics of the filler [1].

The aim of the work is to study the impact of the amount of mineral filler and propylene-octene block copolymer on rheological and mechanical characteristics of extrusion-type polypropylene melts and to choose the composition which suitable for the production of materials with the required properties.

Materials and methods of the research

The filled compositions based on polypropylene (PP) of 21030 mark and blends of polypropylene with 5% w/w propylene-octene block copolymer (POBC) «Vistamaxx 6202» (ExxonMobil) containing 5-50% w/w of mineral filler have been investigated. The calcite concentrate (CC) of 1TK mark (LLC «Tekhnokom») with particle size of 2.5 micrometres (20 micrometres – 1.5%) was used as inexpensive, common and affordable filler, which contains polyolefin and calcium carbonate treated with stearic acid. Polymer compositions were prepared by mechanical mixing of the components and subsequent granulation in the ЧИ-27x30 extruder. The temperature in the zones of the extruder was 155-210-200-200°C, screw rotation rate – 30 rpm. The viscosity (η) of the melts was measured using MB-2 capillary viscometer in the range of shear stresses ($0.1 \div 5.7$) $\cdot 10^4$ Pa at 230°C. The determination of melt flow index (MFI) was carried out according to GOST 11645-73 (National State Standard) using "IIRT" instrument at 230°C and load of 2.16 kgf. Flow pattern «n» was calculated using tangent tilt of the slope at a given point to the flow curve. The Charpy impact value (kJ/m^2) is calculated by dividing the fracture energy by the cross-section area of the specimen according to GOST 4647-80 (National State Standard). The determination of tensile strength and elongation at break was carried out according to GOST 11262-80 (National State Standard).

Results and discussion

The experiments have shown that the addition of (5-50) % wt. CC in the melt of PP leads to decrease in viscosity of the former throughout the range of concentrations and shear stresses (figure 1). The result obtained differs from the traditional regularities of the flow of the melts filled with solid additions, which typically tend to increase viscosity. This may be explained by the fact that the calcium carbonate particle surface is treated with stearic acid, calcium stearate or coupling agents in an amount of 0.5-3% in order to improve the rheological properties and wetting [16, 17].

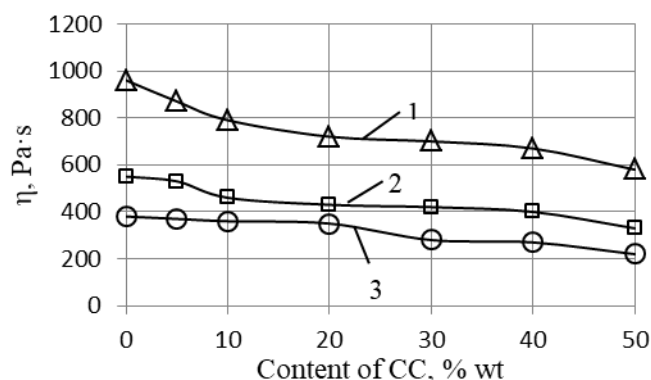


Figure 1. Influence of the content of CC on the viscosity of the polypropylene melt at 230°C and shear stress of $\tau \cdot 10^{-4}$ Pa: 1 – 1.61; 2 – 4.2; 3 – 5.69.

As a result, calcium stearate is formed, which has a non-polar "ends" (figure 2) in the form of stearic acid chain on the surface of the particle [18].

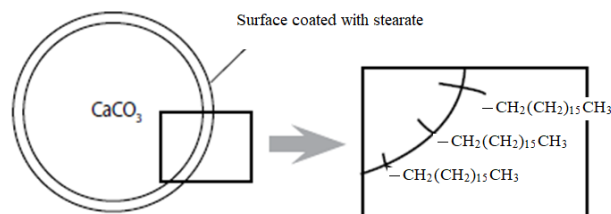


Figure 2. Scheme of CC surface structure.

The formation of the described structure of filler particles improves the compatibility of the melt of hydrophobic PP and filler due to the compatibilizing action of stearic acid chains in the calcium stearate molecule $[\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2\text{OO}^-]_2\text{Ca}^{2+}$ at the interface between their phases and the decrease in the hydrophilicity of calcium carbonate [19]. The viscosity of melts of PP/CC polymer suspensions is determined by two competing factors: emulsifying effect of non-polar "ends" of the acid leads to decrease of viscosity of the melt, and a solid mineral addition provides its increase through the formation of aggregates. The predominant factor is the compatibilizing action of stearic acid chains on the surface of calcium carbonate molecules, which causes the decrease of the melt viscosity in the system. A similar effect of a significant reduction of viscosity has also been described for compositions consisting of polyvinylchloride with hydrophobizing additives based on stearic acid, the activity of which increases in the series: zinc stearate, calcium stearate, stearic acid [18]. The presence of long hydrocarbon chains that have affinity with the macromolecules of PP on the surface of the used filler provides the dispersion homogeneity in the melt and a sharp decrease of the abrasive effect of the filler on the extrusion equipment.

The studied PP compositions filled with CC, as well as the original polypropylene, demonstrate viscosity abnormality, i.e., when the stress or shear rate increases, the viscosity decreases. The behavior of such liquids is described by the polynomial equation: $\tau = \eta \cdot \dot{\gamma}^n$, where n – flow index.

The addition of POBC 5% w/w into the unfilled PP reduces the viscosity of the composition (figure 3). The curves of the compositions PP+50% CC and PP+5% POBC+50% CC almost coincide, that is, the addition of copolymer into filled 50% CC polypropylene does not affect viscosity.

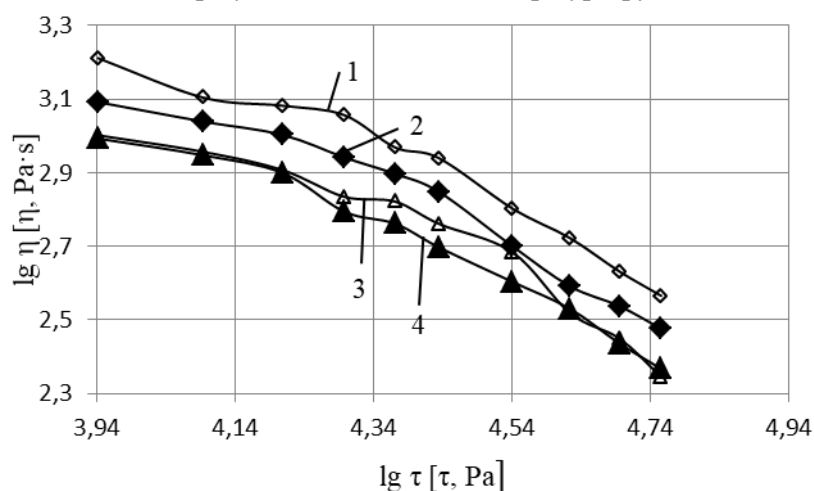


Figure 3. Dependence of the viscosity on the shear stress expressed as logarithmic coordinates for compositions: 1 – PP; 2 – PP+5% POBC; 3 – PP+50% CC; 4 – PP+5% POBC+50% CC.

It has been found that for the compositions based on polypropylene filled with CC, the degree of deviation from the Newtonian flow regime is complex: the value of n decreases from 2.0 (for the initial PP) down to 1.6 and then increases up to 2.3 (table 1). The described dependence is explained by the fact that the index n , as well as the viscosity, depends on many factors with the predominant effect of one of them in each specific case.

Table 1. Effect of calcite content of the concentrate flow mode n of filled compositions

Content of CC, wt.%	$nat \tau \cdot 10^{-4} Pa$	
	5.69	1.61
0	2.0	1.5
5	2.0	1.5
10	1.6	1.2
20	1.9	1.3
30	2.0	1.4
40	2.1	1.5
50	2.3	1.5

It has been found that the increasing of content of CC up to 50% w/w in the composition leads to melt flow index increase from 3.1 g/10 min (without CC) up to 6.6 g/10 min (50% w/w of the filler). With the addition of the POBC 5% w/w as the elastomer in compositions, the curves showing the dependence of melt flow index on the content of CC are similar within the range from 3.4 g / 10 min (without CC) to 6.9 g / 10 min (50% w/w of the filler) (figure 4). It can be explained by appropriate combination of PP and POBC with its plasticizing effect. The plasticizing effect of the composition modified with the elastomer, compared to PP filled with CC 50% w/w, is equal to 4.3%.

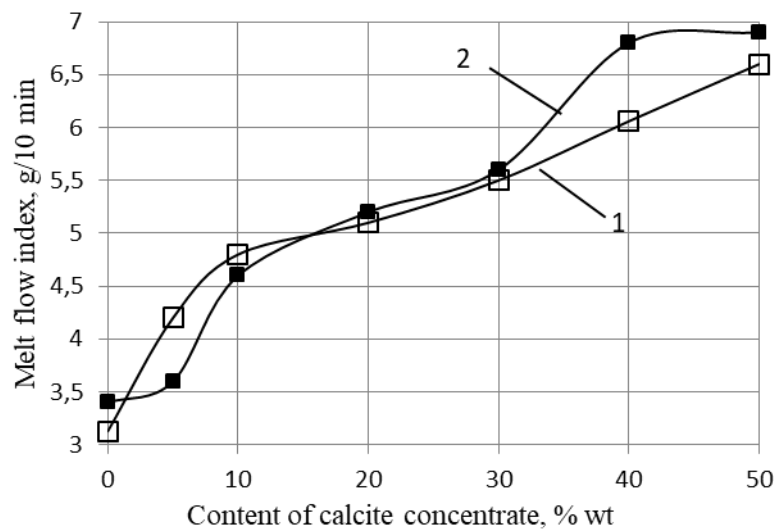


Figure 4. Influence of CC content on melt flow index in compositions:
1–PP+CC; 2 – PP+5%POBC+CC.

The impact strength index characterizes the strength of the material under impact loads. The rubber phase of the modifier combined with the polymer provides a uniform distribution and damping of the impact energy, so that the modified polymer materials withstand a higher impact load [9]. The content of CC 5-10% w/w increases the impact strength probably due to the nucleation effect of PP by CC (figure 5). This effect is enhanced in the presence of POBC as an elasticizing additive.

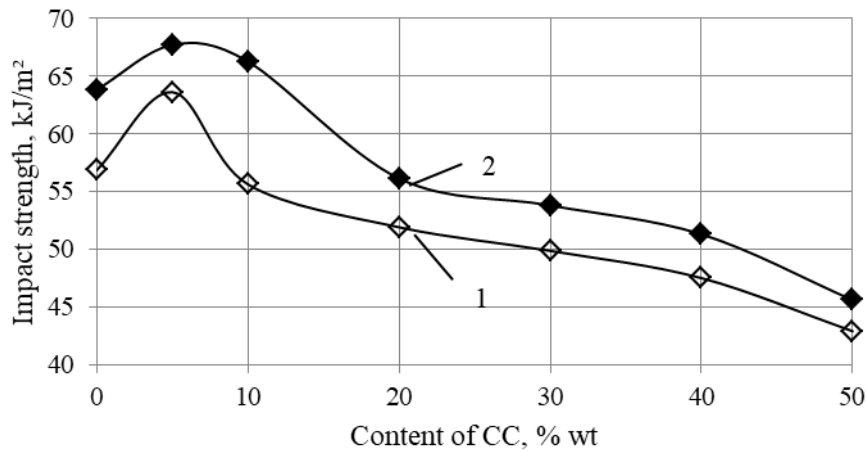


Figure 5. Dependences of the impact strength from the content of CC in composites: 1 – PP+CC; 2 – PP+5%POBC+CC

The addition of POBC5% w/w increases the elongation from 112% to 140% and practically does not change the strength of the composite (figure 6).

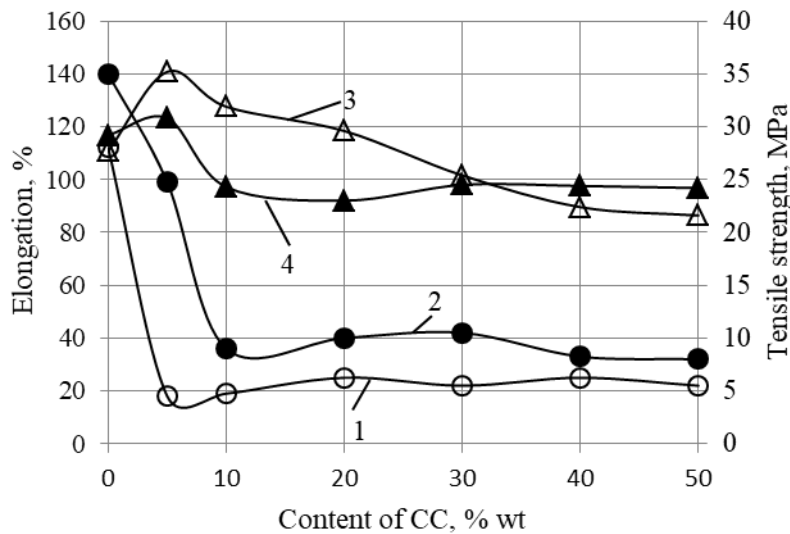


Figure 6. Dependences of the elongation (1,2) and tensile strength (3, 4) from the content of CC in composites: 1,3 – PP+CC; 2,4 – PP+5%POBC+CC

The addition of CC up to 10% w/w into compositions with 5% w/w POBC and without it leads to a decrease of elongation by 74% and 82% respectively. Further increasing of CC content does not lead to significant change of these indexes. The strength of the compositions with 5% w/w POBC with the content of CC 10-50% w/w does not change, while the strength of the composition PP+CC is reduced by 39%.

Conclusion

It has been found that the addition of calcite concentrate 5-50% w/w allows regulation the rheological properties of polypropylene-based composition melts. It was established that the increasing of the amount of the filler up to 50% w/w in the PP based composition led to decrease of its melt viscosity by 40% comparing with initial polymer melt. This may be explained by the

plasticization effect of stearic acid, which is commonly used to treat the surface of calcite concentrate. The addition of a propylene-octene block copolymer as a modifying additive makes it possible to produce high-filled materials that are more resistant to impact loading. The increasing the calcite concentrate content up to 10% w/w increases the impact strength by 10% compared with the initial polypropylene. Further increasing of calcite concentrate content up to 20 % led to decrease impact strength almost to the value for the initial polypropylene, at not critical decrease in tensile strength. Elongation of compositions is higher with the presence of block copolymer. The developed compositions with propylene-octene block copolymer as a modifying additive can be used for production of automotive details.

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